



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B05D 3/06, 3/10, 5/00, C03C 17/28,</b> <b>17/30, 17/32, C08J 7/04, 7/06, C23C</b> <b>26/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/42452</b>  <b>(43) International Publication Date:</b> 1 October 1998 (01.10.98)
<b>(21) International Application Number:</b> PCT/AU98/00185  <b>(22) International Filing Date:</b> 20 March 1998 (20.03.98)  <b>(30) Priority Data:</b> PO 5789                      20 March 1997 (20.03.97)                      AU  <b>(71) Applicant (for all designated States except US):</b> UNISEARCH LIMITED [AU/AU]; 221-227 Anzac Parade, Kensington, NSW 2033 (AU).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> LAMB, Robert, Nor- man [AU/AU]; 9 Gamut Road, Engadine, NSW 2233 (AU). ZHANG, Hua [CN/AU]; 1/1 Templeman Crescent, Hillsdale, NSW 2036 (AU). RASTON, Colin, Llewellyn [AU/AU]; 18 Leumear Street, East Oakleigh, VIC 3168 (AU).  <b>(74) Agent:</b> F.B. RICE & CO.; 605 Darling Street, Balmain, NSW 2041 (AU).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> HYDROPHOBIC FILMS		
<b>(57) Abstract</b>  A method of applying a hydrophobic film to a surface, the method comprising the steps of (a) optionally modifying particles to be coated on the surface so as to form functional groups thereon; (b) applying particles having functional groups thereon to the surface to be coated; and (c) treating the applied particles such that the particles are bound together and to the surface by chemical cross-linking of the functional groups on the particles. The method may further include the addition of a non-silicone polymer to the particles prior to step (b) to assist in the formation of the film.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## Hydrophobic films

### Technical Field

This invention relates to the technology of protective coatings. In particular, the invention relates to film-coating materials which have a low propensity to wet and to methods for making the films. Water resistant or water proof coatings, as well as being useful for water proofing various types of surfaces, can also render such surfaces resistant to icing and fouling. The coatings can also render protected surfaces resistant from attachment by water soluble electrolytes such as acids and alkalies, and from microorganisms.

### Background Art

It is well understood that the wettability of various materials is dependent on both the physical and chemical heterogeneity of the material. The notion of using the contact angle  $\theta$  made by a droplet of liquid on a surface of a solid as a quantitative measure of the wetting ability of the particular solid has also long been well understood. If the liquid spreads completely across a surface and forms a film, the contact angle  $\theta$  is  $0^\circ$ . If there is any degree of beading of the liquid on the surface of the solid, the surface is considered non-wetting.

For water, where the contact angle is greater than  $0^\circ$ , the solid is considered hydrophobic. Examples of materials on which liquid droplets have high contact angles, include water on paraffin which has a contact angle of about  $107^\circ$  and mercury on soda-lime glass which has a contact angle of about  $140^\circ$ .

In the past, surfaces have been protected against encrustation, corrosion, icing and fouling by means of coatings containing polymer films, hydrophobic solid fillers and hydrophobic liquids. One disadvantage of the use of such coatings is that they do not achieve multi-purpose protection since they are not generally versatile enough to protect against damage from a variety of causes.

International Application No WO 94/09074 discloses a multi-purpose solid surface modifier which comprises a composition containing a highly dispersed hydrophobic powder, a silicone liquid, a solvent, and an adhesive for binding the powder together and to the surface. The modifier is described as being effective in imparting water repellent, anti-fouling, anti-icing, anti-corrosive and anti-friction properties to various surfaces. Although the

specification describes exceptionally good experimental results, allegedly providing contact angles in some cases in excess of  $175^\circ$ , in practice it is very difficult to accurately measure contact angle data in excess of  $165^\circ$ .

The present inventors have now developed methods of producing hydrophobic films that are an improvement over the prior art methods. The present invention arises in part from the realisation that the hydrophobicity of a surface coating is determined by two factors, the first being the chemical properties of the material making up the hydrophobic coating or film, and the second being the physical surface conditions.

#### Disclosure of Invention

In a first aspect, the present invention consists in a method of applying an hydrophobic film to a surface, the method comprising the steps of:

- (a) optionally modifying particles to be coated on the surface so as to form functional groups thereon;
- (b) applying particles having functional groups thereon to the surface to be coated; and
- (c) treating the applied particles such that the particles are bound together and to the surface by chemical cross-linking of the functional groups on the particles.

In a second aspect, the present invention consists in a method of applying an hydrophobic film to a surface, the method comprising the steps of:

- (a) optionally modifying particles to be coated on the surface so as to form functional groups thereon;
- (b) mixing particles having functional groups thereon with a non-silicone polymer reactive to the functional groups on the particles;
- (c) applying the mixture of particles and the non-silicone polymer to the surface to be coated; and
- (d) treating the applied particles and non-silicone polymer such that the particles are bound together and to the surface by chemical cross-linking of the functional groups on the particles.

In a preferred embodiment of the first and second aspects of the present invention, the particles are silica particles, preferably having a diameter of between 20 to 100 nm. Silica is cheap and is readily available as a commercial powdered product, known as aerosil flamed silica, whose powder particles are of a suitable size. Although silica and silica-based

particles are preferred, other materials of hydrophobic character which can be prepared in a sufficiently small particulate size could be used. Examples include oxides such as titanium dioxide.

5 The optional modifying step can be any means to form active functional groups that will allow the particles to chemically bond or cross-link to each other and to the surface to be coated. The present inventors have found that when using silica particles, silylalkylmethacrylate groups such as silylpropylmethacrylate (or related) functional groups, or a mixture of those functional groups and passive silylalkyl groups are particularly  
10 suitable. The methacrylate functional groups act as centres for chemically linking the particles. There are also silica particles commercially available that have suitable functional groups thereon such that step (a) can be optional.

15 Chemical cross-linking of the functional groups on the particles may be achieved by the addition of a copolymerisation monomer, such as styrene, to link methacrylate functional groups from one particle to methacrylate functional groups of another.

20 Alternatively, cross-linking of the particles is also possible without the use of monomers, if contact between methacrylate groups from different particles is favourable. It will be appreciated that this will depend on the length of the alkyl chain of the functional group.

Either type of cross-linking can be activated photolytically by means of ultra-violet radiation or by using a radical initiator such as benzoyl peroxide or diethoxyacetophenol.

25 Preferably, the particles (and the polymer, when used) are applied to the surface in a slurry. This can be achieved using a solvent, preferably an organic solvent. One solvent found to be particularly suitable for silica particles is hexane. It will be appreciated, however, that other solvents would also be suitable.

30 The present inventors have found that the cross-linking of the particles when applied to a surface results in the attachment of the particles on the surface thereby forming a hydrophobic film.

In order to obtain a more durable coating, the use of a non-silicone polymer is preferred. A particularly suitable non-silicone polymer is  
35 polyurethane. Preferably, the polyurethane is formed by the reaction of di- or poly-isocyanates with polyols. Isocyanates may react, under suitable

conditions, with the active hydrogen atoms of the urethane linkages to form biuret.

In a preferred method, methylene bis(phenyl isocyanate) (MDI) was chosen to react with polydimethylsiloxane (PDMS) with hydroxyl groups terminated or 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol. The produced  
5 prepolymer has some free isocyanate groups on the chain. Toluene or ethyl acetate can be used as suitable solvents. The prepolymer is mixed with silica powder so that the isocyanate groups on the prepolymer can react with the silanol groups on the powder surface to chemically bond the particles  
10 together and to the surface to be coated.

The method of the present invention produces hydrophobic films with a contact angle of water of at least 150°, preferably at least 160°, and most preferably about 165°.

In a third aspect, the present invention consists in an object having at  
15 least a portion of its surface coated with a hydrophobic film applied by the method according to the first or second aspects of the present invention.

In a fourth aspect, the present invention consists in the use of the methods according to the first or second aspects of the present invention to coat at least part of the surface of an object.

20 The surfaces to be treated can include metals, alloys, glasses, papers, ceramics, polymers, composites, and other materials. The surface treatment can be used to inhibit corrosion, formation of crystallisation centres in water pipe lines, closed heat exchangers, tubular boilers, chillers and refrigerators which utilise water, brine solutions, inorganic acids, alkalies, other  
25 electrolytes, and other corrosive fluids as coolants. The treatment can be used to prevent icing on surfaces, to produce anti-gripping hydrophobic coatings for aboveground fixed facilities such as buildings and other structures, to provide anti-icing and anti-corrosion coatings for aircraft; or to provide anti-icing, anti-fouling and anti-corrosion coatings for maritime and  
30 inland waterway vessels.

Other uses include to improve the resistance of metallic roofs to microflora colonisation; to provide water resistance, waterproofing, and ecological protection to slate and tile; to provide ecologically sound rubberoid and bitumen roofing felt; to provide water and moisture repellent  
35 cork material from paper, container board polyurethane foam and shavings.

The coating may be used for extending the survivability, performance, and reliability of instruments and equipment.

Other uses include to protect granular construction materials including cement, alabaster and chalk for long-term storage, particularly in high humidity regions; extend the life cycle of ferro-concrete, concrete stone, brick, concrete cinder block and wooden structures and buildings exposed to weather conditions and microorganisms; protect frescoes, mouldings, buildings of architectural significance, gypsum structures, church and mosque domes, works of art and manuscripts from atmospheric moisture and microorganisms.

Still other uses envisaged include to reduce drag for vessels such as canoes, yachts, ships, and other watercraft; improve the performance, reliability and corrosion resistance of cooling systems in internal combustion engines utilising closed heat exchangers having liquid heat transfer agents; provide anti-corrosive and anti-icing coatings for undercarriages of vehicles such as tractors and combines and for agricultural machinery in general. The coating may reduce labor intensity and improve product quality for laminated plastic products by reducing mechanical adhesion between the surfaces of compression moulds, punches, dies and product surfaces; assist the uniform distribution of dispersed fillers, such as wool, carbon fibres, fibreglass, artificial fibres, both in solution and suspension; encapsulate hydrophilic liquids including toxic liquids; moisture seal materials; provide "dry water" fire fighting materials; provide surfaces for facilitating pipeline transfer of granular material such as ore, coke, fertilisers or coal.

The film according to the present invention may also be used to waterproof building foundations and structures and radioactive waste storage facilities; extend the operating service life of water cooling towers; protect railroad ties from microflora; provide anti-icing coatings for cooling chambers, refrigerators and chillers; extend the life cycle of hydroelectric power dams; improve the efficiency of wind driven motors; improve performance characteristics of concrete and asphalt in open roadways, highways and thoroughfares; increase the life cycle of automobile tires; adsorb ions of heavy metals and radionuclides; provide anti-abrasive lubricants for ball bearings and other working parts; provide water repellent footwear; waterproof electric motors and electric insulators; waterproof pressurised suits such as diving suits.

Other uses include to conserve paper, books, securities and documents in archives and storage facilities; provide hydrophobic black paste used for waterproof ink in pens; provide hydrophobic denim; provide hydrophobic tents, clothing, umbrellas, raincoats, and suits; provide hydrophobic funnel  
5 filters for use with gasoline and petroleum products; provide hydrophobic sails; provide hydrophobic fishing nets; waterproof fur products; render wallpaper water resistant; conserve dye colours; provide skin protection from burns, acids, bases, other electrolytes, rocket fuels, highly toxic materials and flammable solutions; provide hydrophobic foam for ecological protection of  
10 the atmosphere and fauna and flora against accidental spills of highly toxic poisons and rocket fuels; protect electric train current collectors from ice and corrosion; provide de-icing of airport runways; preserve vegetables and fruits under long-term storage; provide water, moisture and acid resistant footwear; provide waterproofing of printed circuit boards; provide waterproof  
15 lubricants to improve sky slip; localise vaporisation of corrosive fluids in emergencies; improve longevity and performance reliability of pumps and pipelines carrying inorganic acids, alkalies and other corrosive media; encapsulate acid, base, other electrolyte and other corrosive solutions as well as hydrocarbons for transport and storage; provide hydrophobic anti-  
20 agglomeration agents; preserve instruments, equipment and devices by means of conservation lubricants; and protect radio repeater and radar antennas from corrosion and icing

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will  
25 be understood to imply the inclusion of a stated element or integer or group of elements or integers but not the exclusion of any other element or integer or group of elements or integers.

In order that the present invention may be more clearly understood, preferred forms will be described with reference to the following examples  
30 and the accompanying drawings.



### Brief Description of Drawings

Figure 1 shows a XPS spectrum of a powder-only coating;

Figure 2 shows a XPS spectrum of a powder-polymer mixture coating;

Figure 3 shows a SIMS spectrum of a microbiological test sample of  
5 powder-polymer mixture coating before washing; and

Figure 4 shows a SIMS spectrum of a microbiological test sample of  
powder-polymer mixture coating after washing.

### Modes for Carrying Out the Invention

In one preferred method, silica powder is treated with a  
10 trimethoxysilylalkylmethacrylate such as trimethoxysilylpropylmethacrylate  
(or a related compound) and subsequently treated with  
trimethoxysilylalkane. The treatment with the  
trimethoxysilylpropylmethacrylate bonds silylpropylmethacrylate groups to  
the silica. The treatment with trimethoxysilylalkane bonds passive  
15 silylalkane groups to the silica which increase the hydrophobicity of the  
silica particle.

Alternatively, both the trimethoxysilylpropylmethacrylate and the  
trimethoxysilylalkane can be used simultaneously to attach the necessary  
groups to the silica.

20 The modified silica particles are then placed in a suitable solvent. The  
particles may be suitably dispersed in a slurry in hexane, for example. The  
slurry can be stirred and sonicated at 40 Hz to improve the dispersion of the  
particles in the slurry. A suitable surface is then coated with the slurry and  
the slurry is treated so that the particles cross-link to bind themselves  
25 together and to the surface itself.

The cross-linking may be achieved by the addition of a co-  
polymerisation monomer such as styrene to link the functional methacrylate  
groups from one particle to functional methacrylate groups of another.

In an alternative embodiment, cross-linking of the particles may be  
30 possible without the use of monomers if contact between methacrylate  
groups from different particles is favourable. This will depend on the length  
of the alkyl chain in the silylalkylmethacrylate group.

Cross-linking can be activated either photolytically using ultra-violet  
radiation or by using a radical initiator such as benzoylperoxide or  
35 diethoxyacetophenol.

The balance between the ratio of functional groups to passive groups on the silica particles should be such to optimise the linking of the particles and thus the mechanical strength of the coating whilst maintaining sufficient passive groups to optimise the hydrophobicity of the coating.

5       The alkyl chain linking the silyl groups and the methacrylate functional group also has a bearing on the characteristics of the coating, and whether cross-linking is possible without the use of monomers.

UVsorbors may be used to facilitate the curing of the films under ultra-violet light if cross-linking is activated photolytically.

10       The preferred length for the chemical bond connecting the individual particles is about 3Å.

#### PREPARATION OF HYDROPHOBIC FILMS

Several steps to improve the hydrophobicity and durability of the film were carried out. These steps included using fumed silica powder to produce  
15       rough surface in order to increase hydrophobicity, and employing non-silicone polymer (adhesive) to improve the durability of the film.

##### **Method I - powder-only deposition**

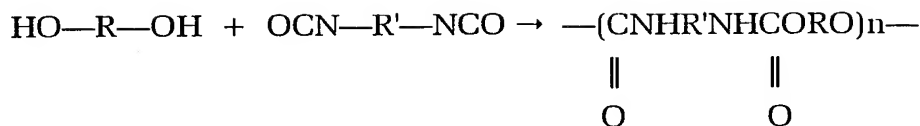
This method involves a slurry of a known concentration of silica powder in hexane at concentration of 2.0 - 2.7% (wt) powder, which was left  
20       in an ultrasonic bath to ensure dispersion and aggregate breakdown, and the slurry was then deposited onto a spinning substrate at a spinning rate of from 500 - 2000 rpm. Different concentrations of the slurry and different spinning speeds were investigated to obtain an optimal hydrophobic film with the highest correct angle.

25       By using this technique, it was possible to obtain a film with contact angle of water approximately 165°. The durability of the film, however, was not ideal in all situations.

##### **Method II - powder and polymer mixture deposition**

To improve the durability of the hydrophobic film, polyurethane was  
30       introduced to act as the adhesive which further links the silica powder together by chemical bonding.

Polyurethane are polymers formed by the reaction of di- or poly-isocyanates with polyols:

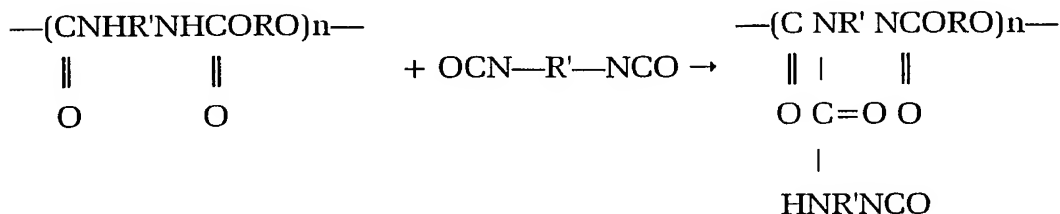


5

polyol + diisocyanate → polyurethane

Isocyanates may react, under suitable conditions, with the active hydrogen atoms of the urethane linkages to form biuret.

10



15

polyurethane + isocyanate → biuret

The method involved preparing prepolymer by reacting polyol with stoichiometrical excess of diisocyanates so as to leave some free isocyanate groups on the prepolymer's chain. The synthesised prepolyurethane then reacts with silanol groups on hydrophilic powder surface to make powder and polymer chemically linked together.

The following examples describe more specific methods of bonding silica powder particles together by polyurethane. In a preferred method, 125 grams of methylene bis(phenyl isocyanate) (MDI) was chosen to react with 75 grams of polydimethylsiloxane (PDMS) with hydroxyl groups terminated (viscosity of 90-150 cst) or 121 grams of 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol in the presence of 1-10% (wt) of diethanolamine as the catalyst. The produced prepolymer has some free isocyanate groups on the chain. Toluene or ethyl acetate was chosen as the solvent, making a concentration as 20-50% (wt) of polymer. The prepolymer was mixed with hydrophilic silica powder (1:1 - 1:2% wt/wt) so that the isocyanate groups on the prepolymer can react with the silanol groups on the powder surface to chemically bond the particles together and to the surface.

The substrates used for method I and method II were rubber, aluminium plates and glass plates.

By using this method, it is possible to obtain a hydrophobic film with the contact angle of water of  $160^\circ$  and having good durability.

## 5 **Microbiological Tests**

The test was carried on in a container full of fresh sea water. The substrates with the hydrophobic coatings were immersed in the sea water which was bubbled with air and added with nutrient broth every half month to provide the food for microorganisms present. The test was carried out over three months. At the end of the test, the substrates were taken out of the sea water and washed by flowing water. The growth and accumulation of the marine microorganisms on the substrates were assessed by the coverage and the adhesion of the marine microorganisms.

## **EXPERIMENTAL RESULTS**

### 15 **Contact Angle Measurements**

Contact angle measurement was carried out by using the sessile drop technique due to the ease and accuracy of the method.

The largest contact angle tested for the coatings prepared by method I was  $165^\circ$  and for the coatings prepared by method II was  $160^\circ$ .

### 20 **Durability**

It was found that the durability of the powder and polymer coatings was much better than the powder-only film by which powder is physically bonded together. The findings were reinforced by the microbiological test data after 3 months by putting the films under seawater. The powder-only coatings were partly destroyed due to the weaker physical bonding between the powder and the substrate. During the 3-month test, some of the powder coating was removed from the substrate and floated on the surface of seawater. The polyurethane-powder coatings, however, remained intact, even after microorganisms growing on the film surface were washed off by flowing water.

### 30 **Resistance to Microorganism Attachment**

Due to the improvement of the film durability, the resistant of the coatings to the microbiological growth was also improved. Unlike the powder-only coatings for which some area of the substrate was exposed to the environment during the test, the powder-polymer coatings were firmly bound to the substrate so that all of the substrate was covered by the

resistant substance after prolonged exposure to sea water. After three months, the attached microorganisms were very easily removed from the powder-polymer coatings by flowing water.

#### **Instrumental Analysis of Surface Coatings**

5           Surface analysis technique were used to determine the chemical composition and surface images of the hydrophobic coatings. Figures 1 and 2 are XPS spectra of powder-only coatings and powder-polymer mixture coatings, respectively. Figures 3 and 4 are spectra of SIMS on the microbiological test samples before and after washing by flowing water.  
10       Many hydrocarbon peaks in the spectrum before washing belong to the microorganisms, and after washing the peaks disappear.

          It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the  
15       invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

## CLAIMS:

1. A method of applying an hydrophobic film to a surface, the method comprising the steps of:
  - 5 (a) optionally modifying particles to be coated on the surface so as to form functional groups thereon;
  - (b) applying particles having functional groups thereon to the surface to be coated; and
  - 10 (c) treating the applied particles such that the particles are bound together and to the surface by chemical cross-linking of the functional groups on the particles.
2. A method of applying an hydrophobic film to a surface, the method comprising the steps of:
  - 15 (a) optionally modifying particles to be coated on the surface so as to form functional groups thereon;
  - (b) mixing particles having functional groups thereon with a non-silicone polymer reactive to the functional groups on the particles;
  - (c) applying the mixture of particles and the non-silicone polymer to the surface to be coated; and
  - 20 (d) treating the applied particles and non-silicone polymer such that the particles are bound together and to the surface by chemical cross-linking of the functional groups on the particles.
3. The method according to claim 2 wherein the non-silicone polymer is polyurethane.
4. The method according to claim 3 wherein the polyurethane is formed  
25 by the reaction of di- or poly-isocyanates with polyols.
5. The method according to claim 4 wherein the polyurethane is formed by the reaction of methylene bis(phenyl isocyanate) (MDI) with polydimethylsiloxane (PDMS) with hydroxyl groups terminated or 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol.
- 30 6. The method according to any one of claims 1 to 5 wherein the particles are selected from the group consisting of silica particles, and metal oxides.
7. The method according to claim 6 wherein the particles are silica particles.
8. The method according to claim 6 wherein the metal oxide is titanium  
35 dioxide.

9. The method according to any one of claims 6 to 8 wherein the particles have a diameter of between 20 to 100 nm.
10. The method according to claim 7 wherein the optional modifying step (a) involves generating silylalkylmethacrylate groups such as  
5 silylpropylmethacrylate (or related) functional groups, or a mixture of those functional groups and passive silylalkyl groups on the silica particles.
11. The method according to claim 10 wherein the chemical cross-linking of the functional groups on the silica particles is achieved by the addition of  
10 a copolymerisation monomer, such as styrene, to link methacrylate functional groups from one particle to methacrylate functional groups on another particle.
12. The method according to any one of claims 1 to 11 wherein the cross-linking is activated photolytically by means of ultra-violet radiation or by using a radical initiator such as benzoyl peroxide or diethoxyacetophenol.
- 15 13. The method according to any one of claims 1 to 12 wherein the particles and the polymer, if used, are applied to the surface in a slurry.
14. The method according to claim 13 wherein the slurry is in an organic solvent.
15. The method according to claim 14 wherein the solvent is selected from  
20 the group consisting of hexane, toluene, and ethyl acetate.
16. The method according to any one of claims 1 to 15 wherein the coated surface has a contact angle of water of at least 150°, preferably at least 160°, and more preferably about 165°.
17. An object having at least a portion of its surface coated with a  
25 hydrophobic film applied by the method according to any one of claims 1 to 16.
18. Use of the method according to any one of claims 1 to 16 to coat at least part of the surface of an object.

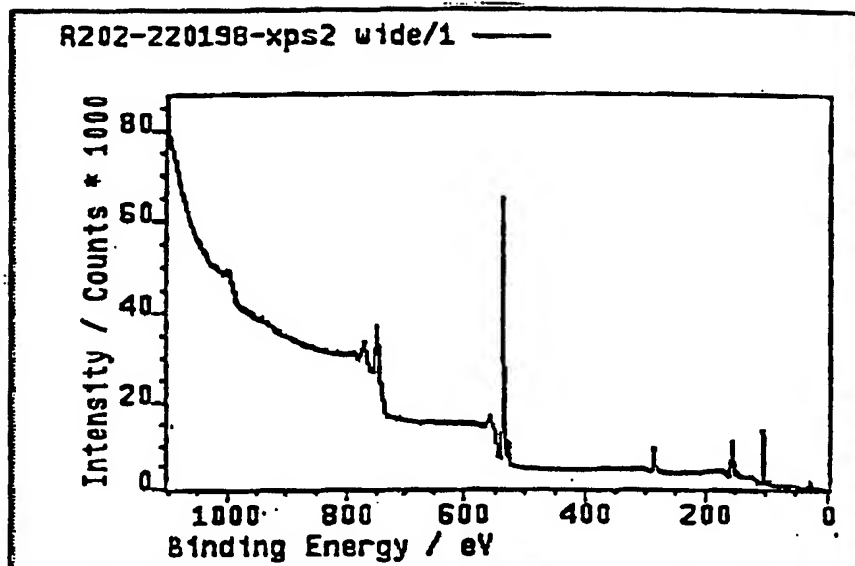


Fig. 1 XPS spectrum of powder only coatings

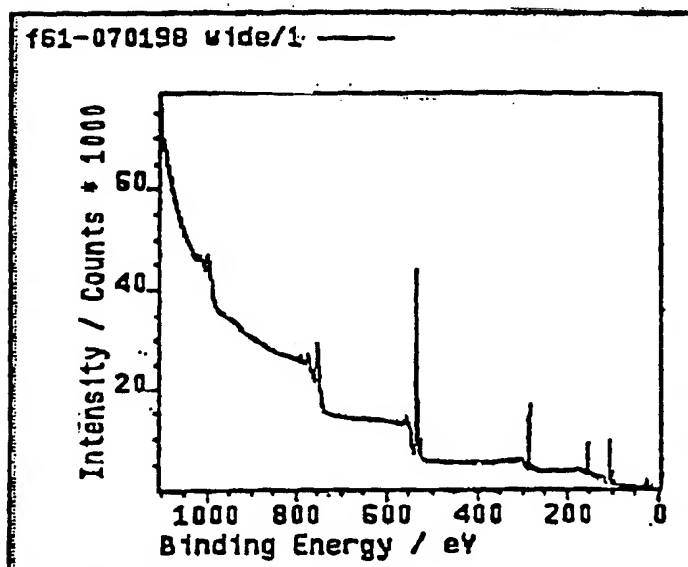


Fig. 2 XPS spectrum of powder polymer mixture coatings



2/2

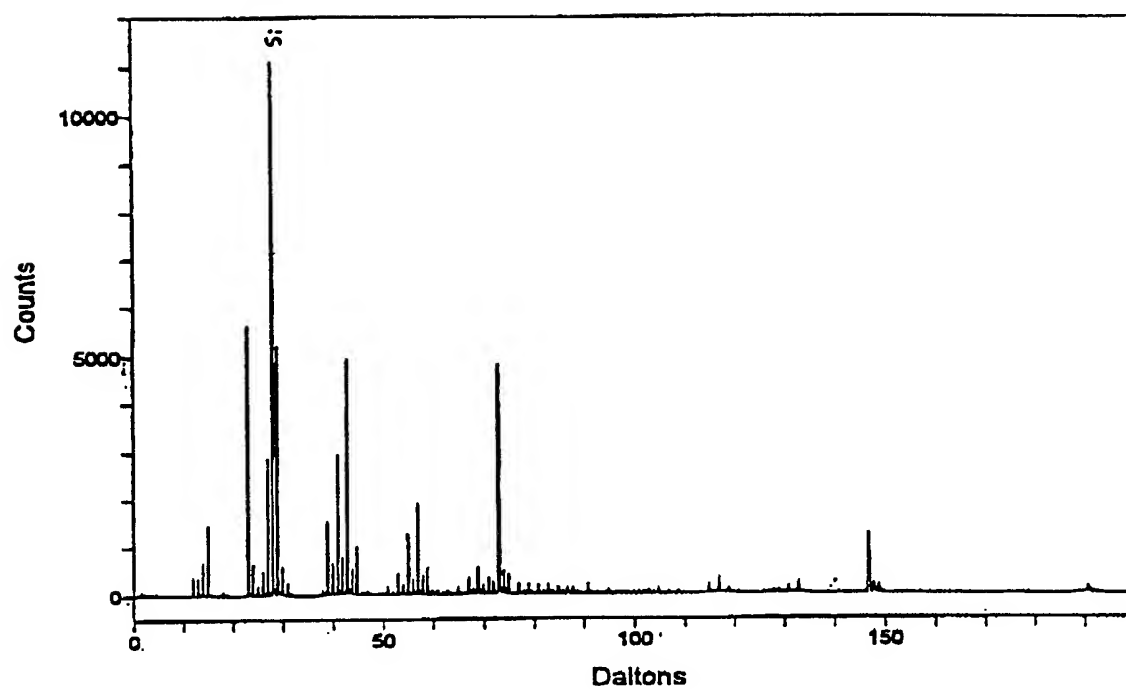


Fig. 2 SIMS spectrum of microbiological test sample before washing

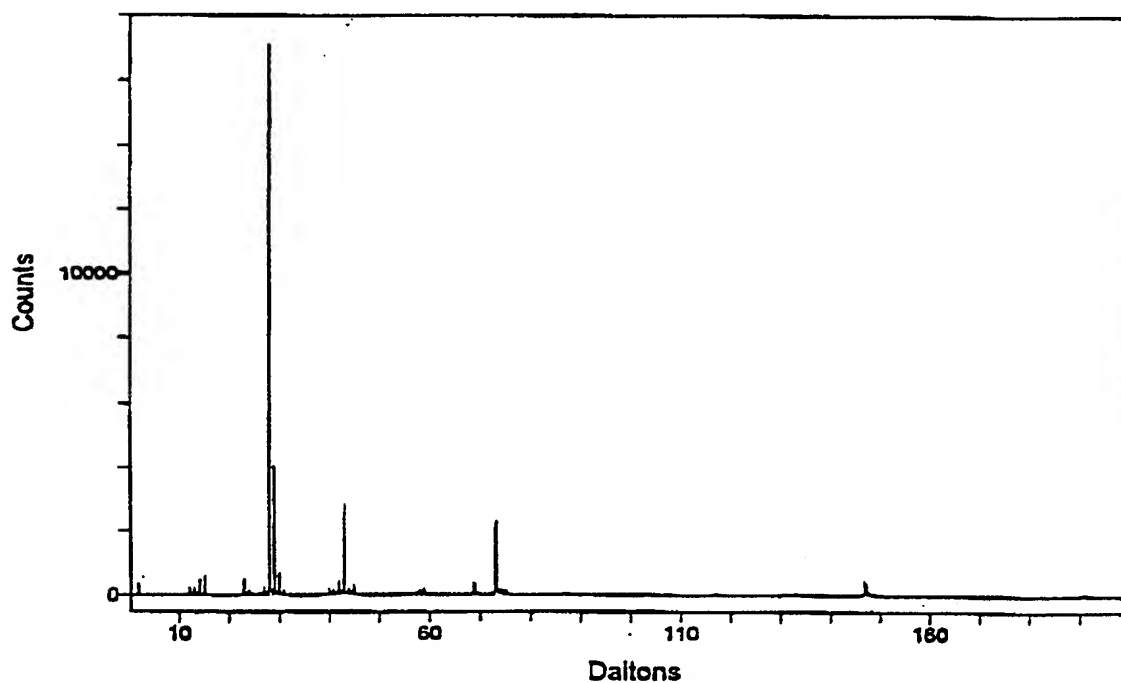


Fig. 3 SIMS spectrum of microbiological test sample after washing

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 98/00185

## A. CLASSIFICATION OF SUBJECT MATTER

Int Cl<sup>6</sup>: B05D 3/06, 3/10, 5/00, C03C 17/28, 17/30, 17/32, C08J 7/04, 7/06, C23C 26/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B05D 3/06, 3/10, 5/00, C03C 17/28, 17/30, 17/32, C08J 7/04, 7/06, C23C 26/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU: as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DERWENT: (B05D 3/06, 3/10 5/00, C03C 17/28, 17/30, 17/32, C08J 7/04, 7/06, C23C 26/00) with keywords  
(Crosslink or X link)

JAPIO: as above

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94/09074 (SMIRNOV et al.) 28 April 1994 In General	1
A	GB 2244489 (ROGERS CORPORATION) 4 December 1991 In General	1
A	Derwent Abstract Accession No. 93-020566/03 Class P73, JP 04 335042 A (DAICEL CHEM IND. LTD.) 24 November 1992 abstract	1

☒ Further documents are listed in the  
continuation of Box C

☒ See patent family annex

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search  
25 May 1998

Date of mailing of the international search report  
10 JUN 1998

Name and mailing address of the ISA/AU  
AUSTRALIAN PATENT OFFICE  
PO BOX 200  
WODEN ACT 2606  
AUSTRALIA  
Facsimile No.: (02) 6285 3929

Authorized officer

L.J. MENZ

Telephone No.: (02) 6283 2431

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/AU 98/00185

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Derwent Abstract Accession No. 95-012038/02 Class A82 G02 (A14) JP 06299088-A (MITSUBISHI RAYON CO. LTD.) 25 October 1994 Abstract	1
A	US 5 260 353 (PALMER et al.) 9 November 1993 In General	1

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International Application No.  
**PCT/AU 98/00185**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
WO	9409074	AU	52997/93	CA	2147144	EP	669963
		US	5747561				
US	5260353	AU	47597/93	BR	9304258	CA	2108505
		CN	1086228	CZ	9302127	EP	593219
		FI	934568	JP	6220251	MX	9306428
		PL	300670	SK	1129/93	ZA	9307088
		US	5362770				